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Electrical Impedance Studies of Acid-Form NAFION Membranes

by

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Electrical conductivity/dielectric relaxation studies of acid form Nafion-117 have been carried out at frequencies from 10 to 10^8 Hz. By direct measurement, it is shown that when "standard" two terminal measurements are made across the thickness of a 0.18 mm film, it is necessary to use frequencies in excess of 10^7 Hz in order to observe the bulk conductivity of the sample. As a consequence, previous reports of a power law dependence for the electrical conductivity are not associated with the bulk electrical conductivity but rather are due to electrode effects and space charge. As confirmation, it is shown that by changing the geometry of the electrodes, the low frequency electrical response of the material is significantly changed.

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ELECTRICAL IMPEDANCE STUDIES OF ACID FORM NAFION MEMBRANES

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ABSTRACT

Electrical conductivity/dielectric relaxation studies of acid form Nafion-117 have been carried out at frequencies from 10 to 10^8 Hz. By direct measurement, it is shown that when "standard" two terminal measurements are made across the thickness of a 0.18 mm film, it is necessary to use frequencies in excess of 10^7 Hz in order to observe the bulk conductivity of the sample. As a consequence, previous reports of a power law dependence for the electrical conductivity are not associated with the bulk electrical conductivity but rather are due to electrode effects and space charge. As confirmation, it is shown that by changing the geometry of the electrodes, the low frequency electrical response of the material is significantly changed.

INTRODUCTION

In a series of papers Mauritz and co-workers [1-5] suggest that the electrical conductivity of Nafion is relatively complicated. They report relaxation peaks in a log-log plot of conductivity versus frequency and a power law dependence of the form:

$$\sigma=\sigma_0\omega^m. \tag{1}$$

Those types of results were reproduced in a recent note by several of the authors [6]. It is shown in the present paper that all of these effects are attributable to electrode effects and space charge and not to the bulk conductivity.

EXPERIMENTAL DETAILS

The samples were films, 0.18 mm thick, of Nafion-117 supplied by E. I. DuPont de Nemours. The samples were pretreated by boiling in a 3% solution of hydrogen peroxide for one hour, washing in boiling water for one hour and soaking in a boiling 1:20 dilute solution of sulfuric acid for one hour. The samples were then dried in a vacuum oven at room temperature before further preparation.

For one set of electrical measurements, the samples were measured in a "standard" two terminal configuration where gold electrodes approximately 6 mm diameter were evaporated onto the faces of the thin film. Difficulties arise for low frequencies and blocking electrodes in the case of Nafion because the electrical conductivity is very high. Consequently, at low frequencies there is

extensive accumulation of charge at blocking electrodes and hence, both electrode effects and space charge are extremely important. In the present work, these "standard" two terminal measurements were carried out over the frequency range 10^6 -10^8 Hz using a Hewlett Packard 4191A RF Impedance Analyzer. The measurements were carried out on a portion of a previously measured, pre-treated sample in ambient atmosphere, that is at about 50% humidity.

For the second set of electrical measurements, the geometry was changed in order to minimize the effects of the electrodes and space charge. Specifically, measurements were made along the thin film rather than perpendicular to it. Strips of Nafion approximately 3 cm long, 1 cm wide and 0.18 mm thick were cut. Gold electrodes were evaporated onto the ends leaving a strip approximately 2 cm long, 1 cm wide and 0.18 mm thick. The equivalent parallel capacitance and resistance of the sample were then determined using both a CGA-83 Capacitance bridge (10-10^5 Hz) and a Hewlett Packard 4194A (100 Hz-40 MHz) Impedance/Gain-Phase Analyzer. For these lower frequency measurements, the samples were suspended above distilled water in an enclosed space so that the measurements were carried out at 100% relative humidity.

All data were then transformed to the apparent complex dielectric constant, $\varepsilon^*=\varepsilon'-j\varepsilon''$, using the appropriate geometrical factors. Finally, the results were transformed to the electrical conductivity, σ, via:

$$\sigma = \varepsilon_0\varepsilon''\omega \qquad (2)$$

It is to be emphasized that this represents an apparent conductivity as it is calculated directly from the equivalent parallel resistance of the sample (real part of the impedance).

RESULTS AND DISCUSSION

High Frequency Measurements

The results of the measurements carried out using the same geometry as in the previous work [1-6] are shown in Figure 1. It is clear that a plateau is reached at about 10^7 Hz. In fact, the value of the conductivity at the plateau is close to that reported for films conditioned at about 50% relative humidity [7,8]. Consequently, it is concluded that effects other than the bulk electrical conductivity, for example electrode effects and space charge, dominate the electrical response across thin films of Nafion at frequencies lower than 10^7 Hz. This disagrees with the previous work where it is suggested that some of the low frequency response of such films, that governed by Eq. (1) where the exponent is significantly different than zero, is indicative of electrical transport [1-6].

Further, the present work was carried out on materials exposed to atmosphere, about 50% relative humidity, and thus these materials are not particularly conductive. Consequently, electrode effects and space charge will extend to even higher frequencies in materials with higher electrical conductivity.

Low Frequency Measurements

The results of the measurements carried out using a different geometry are shown in Figure 2. There is relatively good agreement between the data from the two measuring instruments in the range of frequency overlap. Again, at the lowest frequencies, the apparent conductivity is low, then increases with increasing frequency to a slowly rising plateau beginning at about 1 kHz.

Presumably, the slow rise is due to residual interfacial effects. The data at 5 kHz, at the low end of the plateau, yields a value of 0.061 S/cm which is in excellent agreement with the results of both Zawodzinski et al. [7,8] (who report data at 5 kHz) and Rieke and Vanderborgh [9].

In order to further compare the results with previous work [1-6], the data are shown in the dielectric constant representation in Figure 3. The important feature is that the imaginary part of the dielectric constant is approximately inversely proportional to the reciprocal of the applied frequency since the slope of log(ε'') vs. log(f(Hz)) is about 0.96 . This again shows that the bulk electrical conductivity is not strongly frequency dependent. In fact, such behavior was observed above 1 MHz in some of the previous work [5], though little attention was given to the fact.

Further useful information is obtained via complex impedance plots which are shown in Figure 4. It is clear from the inset that there is a minimum in the imaginary part of the impedance which occurs at about 1 MHz. Presumably, a standard arc would occur at still higher frequencies, corresponding to bulk conductivity in the material. The value of the real part of the impedance at the minimum yields a value of σ=0.073 S/cm. Since the value of the resistance at the minimum is probably closer to the effective dc resistance than is the value at 5 kHz, it is concluded that the electrical conductivity for Nafion conditioned at 100% relative humidity at room temperature is slightly larger than previously reported, namely 0.073 vs. 0.06 S/cm.

The important feature of these low frequency measurements is, of course, that the conductivity plateau and anomalous low frequency features are significantly reduced merely by changing the geometry. Specifically, when the geometry is changed so that the electric field occurs along a long distance rather than a short distance and the electrode area is significantly reduced, the

frequency at which the bulk conductivity becomes dominant is reduced by four decades, from 10^7 Hz to about 10^3 Hz. This represents strong evidence that under conventional measurement conditions the low frequency response of Nafion is dominated by electrode effects and space charge rather than the bulk electrical conductivity.

Further evidence in support of this conclusion has recently been reported by Cahan and Wainright.[10] They have carried out elegant four-terminal measurements on Nafion, which virtually eliminates interfacial effects, and have found that the electrical conductivity is frequency independent from 1 to 10^5 Hz.

CONCLUSIONS

On the basis of electrical conductivity studies of Nafion-117 using an electrode configuration designed to reduce electrode effects and very high frequency measurements using a standard geometry, it is concluded that the previously reported power law dependence for the electrical conductivity and relaxation peaks are not associated with the bulk electrical conductivity but rather are due to electrode effects and space charge. The bulk dc conductivity of Nafion-117 at 100 % humidity is observed to be about 0.073 S/cm, at room temperature.

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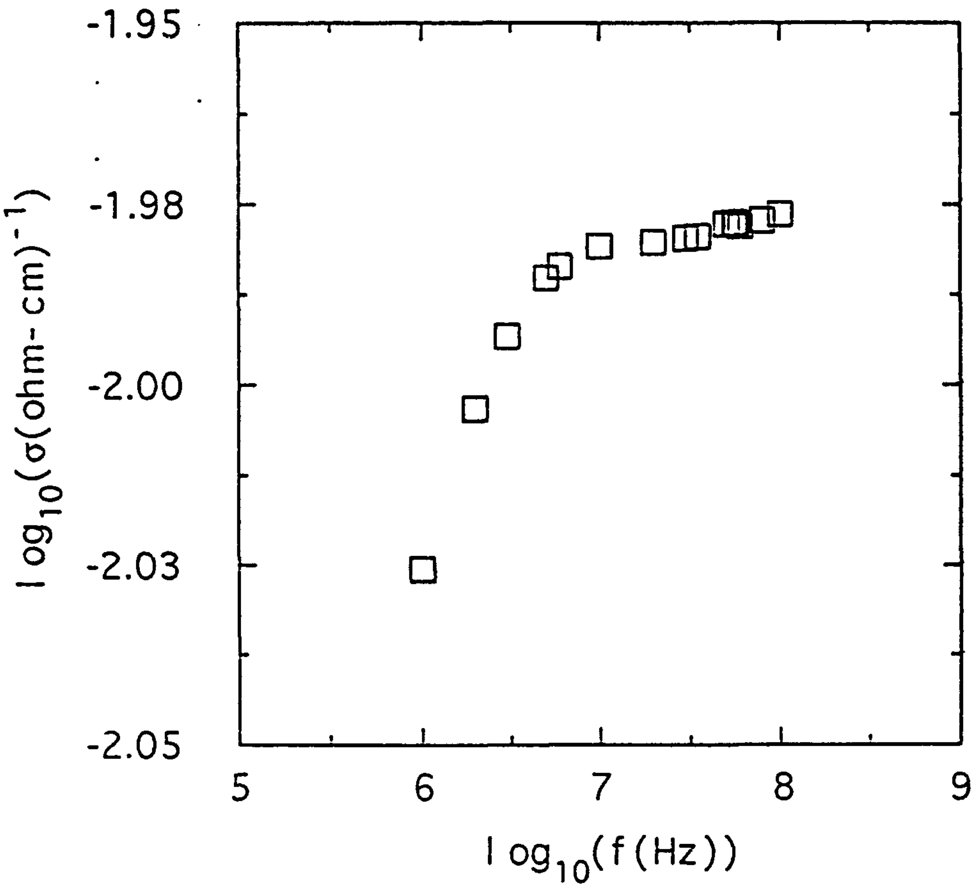
FIGURE CAPTIONS

Figure 1. Electrical conductivity vs. frequency at room temperature (about 295K) and atmospheric pressure for Nafion 117 under ambient conditions (about 50% relative humidity). The measurements are perpendicular to the plane of the film in a standard two terminal geometry. The data are from the Hewlett Packard 4191A RF Impedance Analyzer

Figure 2. Electrical conductivity vs. frequency at room temperature (about 295K) and atmospheric pressure for Nafion 117 conditioned at 100% relative humidity. The measurements are along the plane of the film. The circles are the data from the Hewlett Packard 4194A Impedance/Gain-Phase Analyzer and the triangles are the data from the CGA-83 Capacitance Bridge.

Figure 3. Imaginary part of the dielectric constant vs. frequency at room temperature (about 295K) and atmospheric pressure for Nafion 117 conditioned at 100% relative humidity. The measurements are along the plane of the film. The circles are the data from the Hewlett Packard 4194A Impedance/Gain-Phase Analyzer and the triangles are the data from the CGA-83 Capacitance Bridge.

Figure 4. Complex impedance plot at room temperature (about 295K) and atmospheric pressure for Nafion 117 conditioned at 100% relative humidity. The measurements are along the plane of the film. The circles are the data from the Hewlett Packard 4194A Impedance/Gain-Phase Analyzer and the triangles are the data from the CGA-83 Capacitance Bridge..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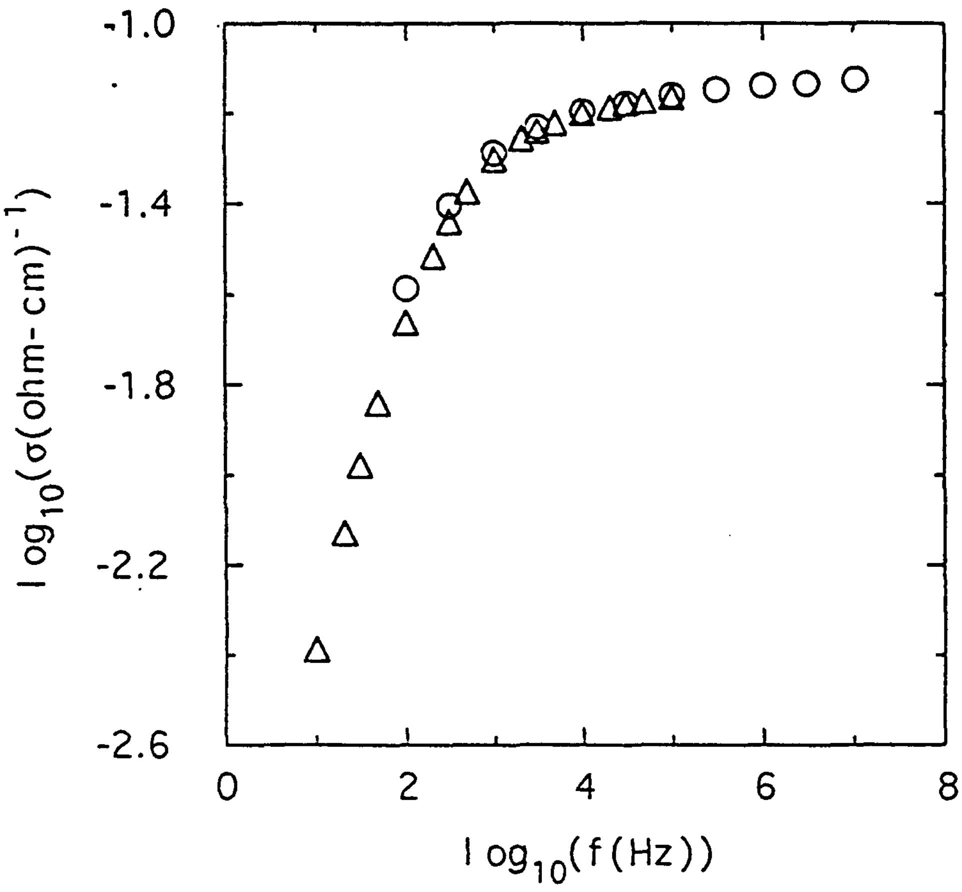
$\log_{10}(f(\text{Hz}))$



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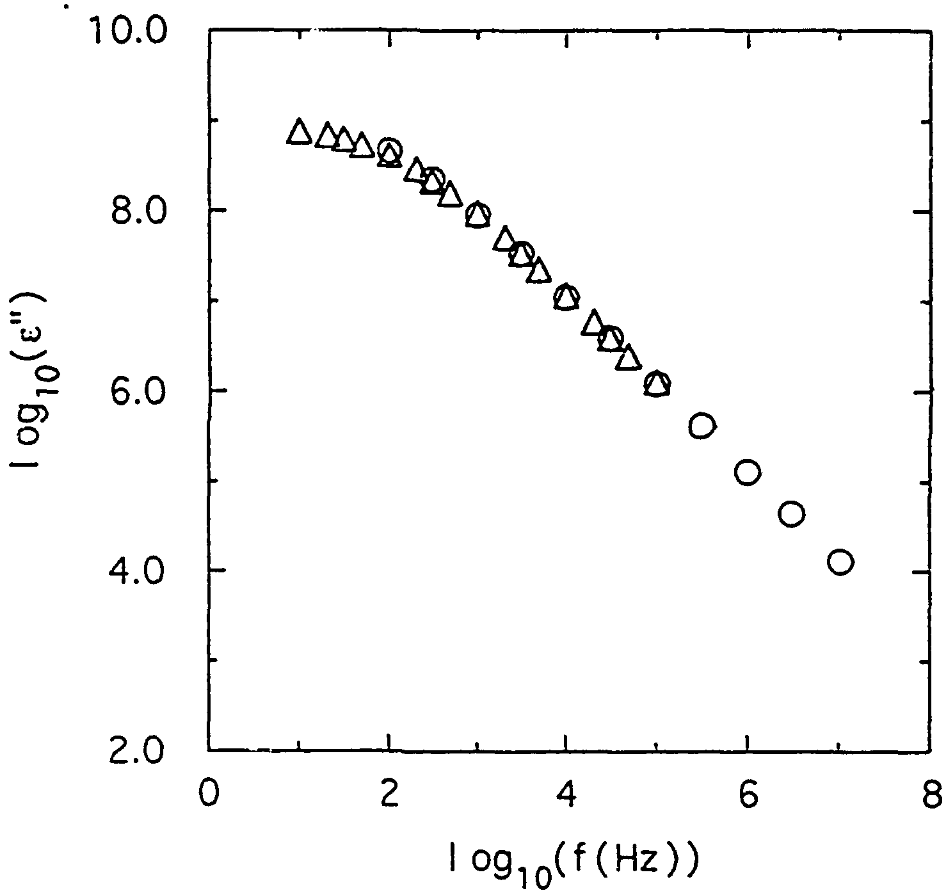
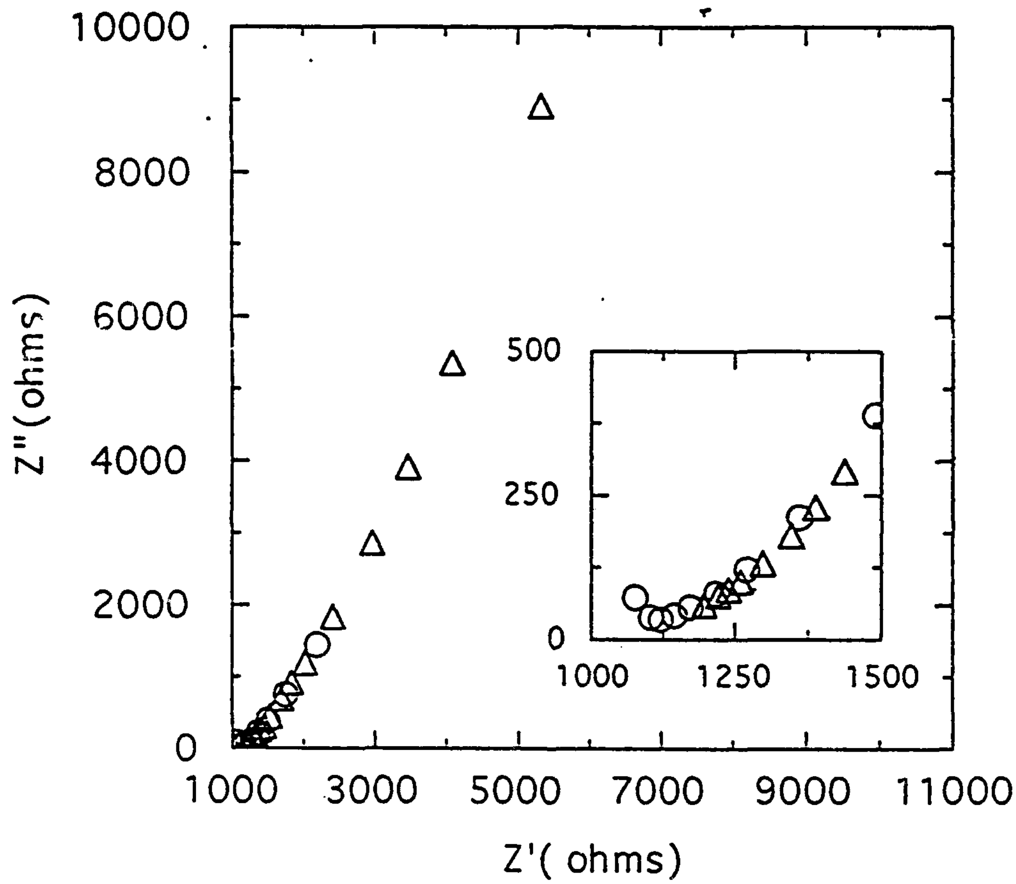


Figure 3



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Z'(ohms)
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1000
1250
1500

Figure 11